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(54) Process for the Production of Titanium Dioxide

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A process for the production of titanium dioxide

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The present invention relates to a process for the production of titanium dioxide by discontinuous digestion of titanium slag with sulphuric acid, production of a titanyl sulphate solution suitable for hydrolysis from the solid digestion cake obtained during digestion, hydrolysis of the titanyl sulphate, separation and calcination of the titanium-containing hydrolyzate, evaporation of the waste acid separated from the hydrolyzate and re-use of the sulphuric acid separated from the evaporated waste acid in the digestion of titanium slag.

The requirement for recycling of sulphuric acid from the TiO_2 production process by the sulphate process is having to be met more and more. In addition to the expected economic disadvantages in comparison with dumping of waste acid in the ocean, the process often encounters technical problems.

A process for working up waste acids is known from DE-A 3 327 769 and is adopted on an industrial scale. Depending on the local condition, however, problems can arise here if the waste acid is to be almost completely recycled.

According to the working up process currently adopted, the waste acid is concentrated, preferably by multi-stage vacuum evaporation, until a 60 to 70% sulphuric acid with a low content of dissolved metal sulphates can be separated by filtration from crystallized metal sulphates.

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5 Weinheim 1979). However, this stage of the process is extremely expensive with respect both to the investment costs and to the energy and maintenance costs.

10 It is accordingly the object of the present invention to propose a method which overcomes the above-mentioned disadvantages of the prior art in an economical manner.

15 This object can surprisingly be achieved by the following combination of measures:

- evaporation of the 60 to 75% sulphuric acid separated from the metal sulphates and containing dissolved metal sulphates under vacuum in horizontal or circulation evaporators at from 120 to 190°C to 76 to 87% H₂SO₄ (based on salt-free sulphuric acid),
- mixing of the ground titanium slag with 95 to 98% sulphuric acid at from 30 to 80°C and addition of the recycled acid at a temperature of from 80 to 190°C, preferably from 100 to 160°C.

20 The present invention accordingly relates to a process for the production of titanium dioxide by discontinuous digestion of titanium slag with sulphuric acid, production of a titanyl sulphate solution suitable for hydrolysis from the solid digestion cake obtained during digestion, hydrolysis of the titanyl sulphate, separation and calcination of the titanium-containing hydrolyzate, evaporation of the waste acid separated from the hydrolyzate and re-use of the sulphuric acid separated from the evaporated waste acid in titanium slag digestion, a 60 to 75% pre-concentrated sulphuric acid being separated from the solid metal sulphates and hydrogen sulphates after

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5 In a particularly desirable embodiment of the process according to the invention, the concentration of the sulphuric acid is advantageously between 87 and 91%, preferably 88 and 90% H₂SO₄ (calculated as solids-free and salt-free acid) at the start of the digestion reaction and
10 from 35 to 70% of the required sulphuric acid is recovered as recycled acid from the process.

The necessary temperatures of the fresh acid and the recycled acid can be lowered according to the invention by grinding the titanium slag more finely.

15 The production of the 76 to 87% acid from 60 to 75% pre-concentrated sulphuric acid is preferably carried out by evaporation at from 120 to 190°C and from 40 to 150 mbar.

20 Horizontal evaporators with tantalum heat exchangers or circulation evaporators are particularly suitable for these evaporation processes not only for reasons of energy consumption.

25 Valuation of the process according to the invention has to consider the fact that secondary energy can be used instead of primary energy for producing the recycled acid and that the investment and maintenance costs are substantially lower compared with the prior art.

The drawing serves to illustrate the process according to the invention.

30 The fresh acid (1) required for the digestion of raw material is mixed in the digestion reactor (3) or in a preceding mixer with the ground titanium slag (2) (optionally with addition of ground ilmenite). The fresh acid should have a temperature of from 30 to 80°C,
35 preferably from 50 to 80°C. The necessary quantity of

5 The metal sulphates are partly in the form of
hydrogen sulphates and contain 60 to 75% sulphuric acid
as moisture. It is therefore advantageous to decompose
this "filter salt" thermally with formation of SO₂ and to
produce therefrom the 95 to 98% sulphuric acid required
as fresh acid. However, reaction with Ca compounds (DE-A
10 3 327 770) or a different harmless elimination process is
also possible.

15 Sulphuric acid losses occur mainly through the filter
salt, but also through the moisture of the solid residues
resulting from raw material digestion, the sulphuric acid
bound in the TiO(OH)₂ and the unavoidable waste water. As
pre-concentrated acid, therefore, only about 40 to 60% of
the sulphuric acid used during digestion can be recovered.
With 60 to 75% H₂SO₄, however, the concentration of this
acid is too low to allow autothermal slag digestion in
20 mixture with the necessary amount of from 95 to 98% fresh
acid.

25 The pre-concentrated acid (15) which still contains
about 3 to 6% by weight of dissolved metal sulphates
therefore must be evaporated in an evaporation II (16) to
76 to 87% H₂SO₄ (as salt-free acid), before it can be
recycled (17) for the digestion of the raw material. The
evaporation II (16) is carried out according to the invention
by vacuum evaporation at 120 to 190°C. Circulation
30 evaporators or horizontal evaporators with tantalum heat
exchangers can be used as evaporator systems. Horizontal
evaporators are preferred owing to the particularly high
specific evaporation capacity (with respect to the
tantalum heat exchanger surface). Preheating of the pre-

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Example 1 (Comparison Example)

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17.5 t of ground titanium slag were mixed with 18 t of metal sulphate-containing recycled acid and with 13.6 t of fresh 96% sulphuric acid (20°C). The digestion reaction was initiated by addition of 1.4 t of water and introduction of 0.6 t of steam. The maximum reaction temperature of 203°C was attained after 10 minutes. After initiation of the reaction, air was blown through the mixture (for 30 minutes at 350 m³/h, then for 7 hours at 20 m³/h). After a maturing time of 7 hours, the digestion cake had a temperature of 169°C. The TiO₂ yield was 95.3%.

The digestion cake was dissolved with a proportion of the sulphuric acid-containing waste water from the hydrolyzate filtration (5.4% by weight H₂SO₄). After working up the titanyl sulphate solution, the mixture was hydrolysed using a further proportion of the sulphuric acid-containing waste water as diluent water.

85 t of waste acid containing 23.2% H₂SO₄ and 29.8% SO₄²⁻(total) were separated from the hydrolyzate filtration process. The waste acid was evaporated in a 2-stage vacuum evaporator until the sulphuric acid (calculated as salt-free acid) had a concentration of 66% H₂SO₄. 31 t of 5 bar steam were used up for evaporating 47.5 t of H₂O.

11.3 t of sulphuric acid-containing filter cake were separated from the metal sulphate-sulphuric acid suspension after cooling to 55°C. The pre-concentrated acid (25.7 t) contained 62.8% of H₂SO₄, 32.4% of H₂O and 4.8% of dissolved metal sulphates.

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being 160°C. The steam consumption for producing 20.0 t of recycled acid was 10 t of 15 bar steam. The 1.3 bar steam for preheating the pre-concentrated sulphuric acid was produced by depressurising the 15 bar steam condensate. In view of the re-use of the 120°C hot steam condensate for steam production, the energy consumption for producing the recycled acid from pre-concentrated acid was 22,700 kJ. 0.6 t of 5 bar steam were also saved when initiating the digestion reaction. An advantage of 33% of the energy requirement was therefore achieved in comparison with the prior art.

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Example 3

17.5 t of ground titanium slag were mixed with 13.6 t of fresh 96% sulphuric acid (75°C). The digestion reaction was initiated by addition of 20.76 t of recycled acid (77.65% of H₂SO₄, 16.57% of H₂O, 5.78% of MeSO₄, corresponding to 82.4% of H₂SO₄ in the salt-free acid) having a temperature of 140°C. Air (350 m³_n/h) was blown through the reaction composition until the maximum temperature of 192°C was attained after 14 minutes. 5 bar steam (180°C, 0.3 t/h for 20 minutes and 20 kg/h for a further 7 hours) was then blown through the reaction composition. After stopping the steam, the temperature of the digestion cake was 172°C and the TiO₂ yield was 95.2%.

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The remainder of the process was carried out as in Example 1. Evaporation II during which 25.7 t of pre-concentrated acid were evaporated to 20.76 t of recycled acid was carried out at 60 mbar in the same horizontal evaporator as in Example 2. The pre-concentrated acid

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Table 1

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	Exp.	Fineness of grinding	T ₁	T ₂	T ₃	T ₄	t
	No.	% by weight < 40 μm	[°C]	[°C]	[°C]	[°C]	[min]
10	1	81	50	110	76	-	-
	2	81	50	140	91	106	36
	3	81	70	140	101	154	67
	4	81	80	140	109	193	37
	5	81	70	160	117	192	23
	6	100	50	120	86	168	42
15	7	100	50	140	95	185	28

The experimental results show that the temperature of the recycled acid can be lower if the titanium slag is ground more finely (Experiment 7) than with a coarser grinding (Experiment 2) achieving approximately the same reaction rate. Also the temperature of the 96% fresh acid can obviously be lowered instead of the temperature of the recycled acid.

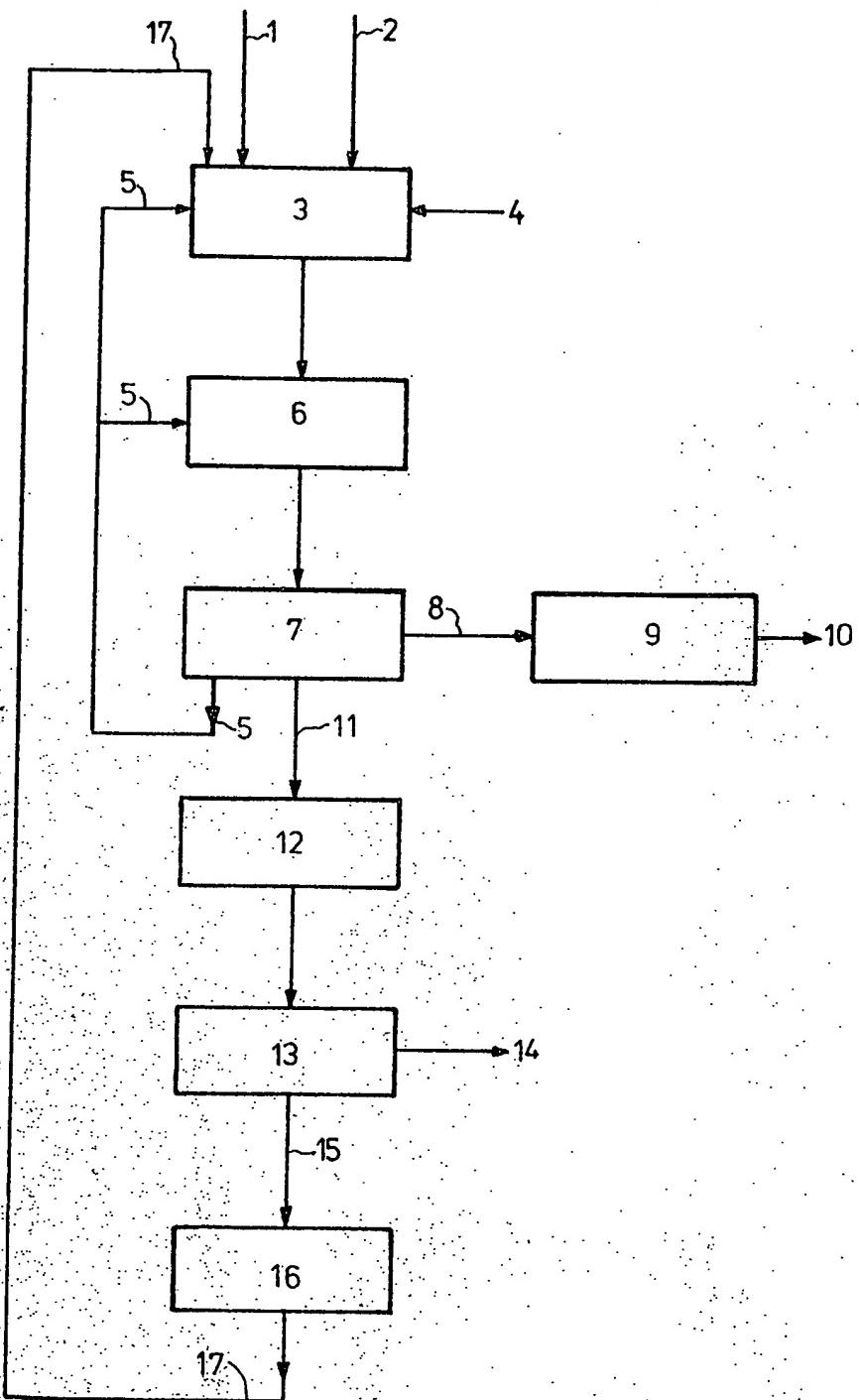
The slower rise in the temperature of the laboratory digestions in comparison with the rise in temperature on an industrial scale is due to the relatively high thermal losses.

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5. A process according to claim 1, 2 or 3, wherein the digestion reaction is initiated by addition of hot 76-to 87%-sulphuric acid ("recycled acid") at from 100 to 160°C.
6. A process according to claim 1, 2 or 3, wherein the concentration of the sulphuric acid is between 87 and 91%, H_2SO_4 (calculated as solids-free and salt-free acid) at the beginning of the digestion reaction and from 35 to 70% of the sulphuric acid required is recovered from the process as recycled acid.
7. A process according to claim 1, 2 or 3, wherein the concentration of the sulphuric acid is between 88 and 90% H_2SO_4 (calculated as solids-free and salt-free acid) at the beginning of the digestion reaction and from 35 to 70% of the sulphuric acid required is recovered from the process as recycled acid.
8. A process according to claim 1, 2 or 3, wherein the production of the 76 to 87% acid from 60 to 75% pre-concentrated sulphuric acid is effected by evaporation at from 120 to 190°C and from 40 to 150 mbar.
9. A process according to claim 1, 2 or 3, wherein the production of the 76 to 87% acid from 60 to 75% pre-concentrated sulphuric acid is effected by evaporation at from 120 to 190°C and from 40 to 150 mbar and a horizontal evaporator with a tantalum heat exchanger is used as evaporator.
10. A process according to claim 1, 2 or 3, wherein the production of the 76 to 87% acid from 60 to 75% pre-concentrated sulphuric



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